Water does partially dissociate on the perfect TiO_2(110) surface: a quantitative structure determination

D.A.Duncan[1], F. Allegretti[1,2] and D.P. Woodruff[1*]

[1]*Physics Department, University of Warwick, Coventry, CV4 7AL, UK*
[2]*Physik Department E20, Technische Universität München, James-Franck Str. 1, München, D-85748, Germany*

Abstract

There has been a long-standing controversy as to whether water can dissociate on perfect areas of a TiO_2(110) surface; most early theoretical work indicated this dissociation was facile, while experiments indicated little or no dissociation. More recently the consensus of most theoretical calculations is that no dissociation occurs. New results presented here, based on analysis of scanned-energy mode photoelectron diffraction data from the OH component of O 1s photoemission, show the coexistence of molecular water and OH species in both atop (OH_t) and bridging (OH_{br}) sites. OH_{br} can arise from reaction with oxygen vacancy defect sites (O_{vac}), but OH_t have only been predicted to arise from dissociation on the perfect areas of the surface. The relative concentrations of OH_t and OH_{br} sites arising from these two dissociation mechanisms are found to be fully consistent with the initial concentration O_{vac} sites, while the associated Ti-O bondlengths of the OH_t and OH_{br} species are found to be 1.85±0.08Å and 1.94±0.07 Å, respectively.

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*Corresponding author. Email address: d.p.woodruff@warwick.ac.uk

The (110) surface of the rutile phase of TiO_2 is the most-studied of all oxide surfaces [1, 2, 3], not least because of the technological importance of titania as a heterogeneous catalyst, and particularly the discovery some 30 years ago of the photochemical production of hydrogen from water over titania [4]. However, despite the importance of this TiO_2/H_2O interaction, aspects of the interaction of water with TiO_2(110) have remained controversial. In particular, for many years most theoretical studies, mainly based on density functional theory (DFT), predicted that dissociation of H_2O on a perfectly-ordered stoichiometric surface should be facile, at least at some coverages, while experiments have generally been interpreted as indicating that this not the case. The appropriate computational methods to tackle this problem correctly have been a source of significant controversy [5, 6, 7, 8, 9], but the most recent calculations favour entirely or mostly molecular adsorption, apparently bringing theory and experiment into agreement [10, 11, 12, 13]. However, the computed energy differences between molecular and dissociated states are small (typically ~0.1 eV or less), and a very recent experimental photoemission study has presented evidence for the presence of a dissociated species on the well-ordered surface at low temperature [14], reopening the question. In contrast to this situation on the perfect surface, it is widely agreed that water dissociation does occur at the surface oxygen vacancy sites of a defected surface; bridging oxygen atom vacancies are replaced by an OH species with the remaining H atoms from the water bonding to adjacent bridging oxygen atoms, leading to a healing of the vacancy and the creation of two bridging hydroxyl (OH_{br}) species (Fig. 1). This process has been predicted in a number of DFT studies and has been observed rather directly by scanning tunnelling microscopy (STM) [15, 16]. On undefected regions of the surface, the same STM experiments show that molecular water is located atop the undercoordinated surface Ti atoms, while scanned-energy photoelectron diffraction (PhD) studies shows the associated Ti-O bondlength to be 2.21 Å [17, 18]. Relatively recent DFT calculations [19] have stressed that on the perfect TiO_2(110) surface, the dissociated state (which appears to be marginally energetically disfavoured [10]) may only be 'pseudo-dissociated' in that the resulting surface species, a hydroxyl species atop a surface Ti atom (OH_t) and an *adjacent* hydroxylated bridging O atom producing an OH_{br} (Fig. 1), may be unable to separate on the surface. Indeed, it is suggested that the detached H atom from the (atop) molecular water may switch rapidly between the OH_t species and the two adjacent bridging O atoms on either side, making it difficult or impossible to identify this process in STM, a technique that detects only a time-average of this switching.

Here we show that using the PhD technique we can not only demonstrate the presence of these coadsorbed OH_{br} and OH_t species as a result of water dissociation, coexistent with intact molecular adsorption, but can also determine the local Ti-O bondlengths of these two species. We find these values to be in excellent agreement with the published DFT results for the dissociated species. As such, we show that the newly-achieved theoretical consensus that water dissociation does not dissociate on the perfect TiO_2(110) surface is not, after all, consistent with experiment. An earlier theoretical treatment [5] indicating that coadsorbed molecular water and dissociated water can coexist on the surface is, however, in agreement with our results.

A key result that underpins our study comes from the investigation by Walle *et al.* [14] of the temperature dependence of O 1s soft X-ray photoelectron spectroscopy (SXPS) data from the TiO_2(110)/water surface. It is well-established that at low temperatures (<~230 K) this spectrum comprises three components, a main peak from the oxide substrate, a second component shifted by ~1.3 eV to higher binding energy associated with surface OH species, and a third peak at a larger chemical shift (~3.5 eV) associated with molecular water. Walle *et al.* showed that the OH component corresponds not only to a state that is stable above room temperature, assigned to the OH_{br} species associated with dissociation at defect sites (e.g. [20]), but also to a second state that desorbs at essentially the same temperature as the molecular water (~240 K), and which has a substantial coverage even on an almost perfect starting surface. The implication is that the additional OH detected at low temperature is the combined OH_{br} + OH_t pseudo-dissociated state predicted by theory, and that recombination of these components leads to desorption below room temperature

In order to establish that this is, indeed, the case, we have applied the PhD technique [21, 22] to this problem. Photoelectron diffraction exploits the coherent interference of the directly emitted component of a photoelectron wavefield arising from a core level of a surface atom with components of the same wavefield elastically scattered by neighbouring atoms. In PhD the photon energy, and hence the photoelectron energy and its associated wavelength, is scanned causing scattering pathways to switch in and out of phase. The resulting modulation spectra of photoemission intensity as a function of energy in fixed directions allows the location of the emitter to be determined, relative to the underlying substrate atoms, through multiple scattering simulations for different model structures. Because the photoelectron

binding energy depends on the bonding environment of the emitter atom, PhD modulation spectra can be extracted from specific spectral components, rendering the technique not only elementally specific, but also chemical-state specific. We have previously applied this method to investigate the adsorption of water on TiO_2(110), but in this earlier study [17, 18] we focussed only on the adsorption geometry of the molecular water species. PhD data were also extracted from the intermediate binding energy peak, but a superficial qualitative analysis suggested that this feature may arise from the oxidic O atoms, and no quantitative analysis was undertaken. There is now ample evidence that this intermediate peak is from surface OH species [14, 20, 23] and with hindsight we now see that the similarity of the PhD from the oxidic and OH oxygen atoms stems from the fact that both of these atoms occupy similar atop and bridging sites relative to the underlying bulk oxide, as we show below. Moreover, our new detailed analysis reveals that while the PhD from the hydroxyl and oxidic O 1s components are, indeed, somewhat similar, there are also important differences. Notice, too, that even SXP spectra from a nominally clean surface typically contain a significant component of the intermediate OH feature due to hydroxylation of the O_{vac} states by the small amount of water in the gas phase under UHV conditions; the O 1s spectrum obtained after removing adsorbed water by heating may therefore appear the same as this 'clean' surface spectrum, but in reality both surfaces have a significant OH_{br} coverage.

Here we present the results of a full quantitative analysis of the O 1s PhD from this hydroxyl component of the earlier data, obtained from the TiO_2(110) surface at ~190 K after exposure to water at lower temperature. Details of the experimental methods are reported in the earlier publications [17, 18]. Briefly, the experiments were conducted in an ultra-high vacuum surface science end-station of BESSY II, equipped for sample cleaning, heating and cooling. Characterisation *in situ* was achieved by low energy electron diffraction (LEED) and by soft-X-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. A clean well-characterised rutile TiO_2(110) surface was prepared which gave a sharp (1x1) LEED pattern and a Ti 2p photoemission spectrum showing only a weak high kinetic energy shoulder. This surface was exposed to ~10^{-6} mbar.s of H_2O at a temperature of 125 K, heated to ~230 K, and held at 190-200 K during measurement of the PhD spectra to avoid multilayer film formation from residual gas-phase water. PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the O 1s peaks at 4 eV steps in photon energy, in the photoelectron energy range of approximately 50-315 eV, in several different emission directions. Each EDC was fitted by a sum of three

chemically-shifted Gaussian peaks (oxide, OH, water), a step, and a template background. The resultant O 1s hydroxyl PhD spectra recorded in some directions were dominated by noise at the higher energies, and these spectra were truncated prior to comparison with theory to reduce the impact of this noise on the *R*-factors (reliability-factors [21, 22]) associated with comparison with theory. Structure determination from the PhD spectra obtained from the OH component was achieved through the use of multiple scattering simulations for trial model structures using computer codes developed by Fritzsche [24, 25, 26]. Structural optimisation to find the best agreement between theory and experiment, as judged by the lowest value of the *R*-factor, was achieved using our normal procedure (e.g. [22, 27]). Specifically, we explored models involving different fractional occupations of OH_{br} and OH_t species, and allowed optimisation of a range of local structural parameters including both Ti-O bondlengths and local near-surface relaxations. A search of all possible lateral positions at all reasonable Ti-O bondlengths for the location of the second OH species (coadsorbed with OH_{br}), showed the OH_t site to give much the best fit to the PhD data.

The structure yielding the lowest *R*-factor value (0.31) for a set of spectra recorded in five different directions (Fig. 2) was found to correspond to an OH_t:OH_{br} co-occupation ratio of 30:70. The OH_t species has a Ti-O bondlength of 1.85±0.08 Å, while for the OH_{br} species this bondlength is 1.94±0.07 Å. This latter value is in excellent agreement with the value of 1.97±0.05 Å found by Unterberger *et al*. [23] using the same PhD technique to study a surface hydroxylated by exposure to atomic hydrogen, and thus containing only OH_{br} species. These bondlengths are fully consistent with strong chemisorption and are much shorter than the value associated with molecular water in the Ti-atop site on this surface (2.21±0.02 Å) [17, 18]. Few of the published DFT calculations on this system quote bondlength values for comparison with experiment; for example, ref. [10] gives perfect agreement with experiment for the Ti-O_{water} bondlength, but provides no details of the dissociated state. Menetrey *et al.* [28] find a slightly longer value for Ti-O_{water} of 2.28 Å, but also report the Ti-OH_t bondlength to be 1.85 Å. These authors do not quote the Ti-OH_{br} bondlength on the perfect surface, but on the initially-defected surface they give a value of 2.09 Å; this is quite similar to the value of 2.04 Å obtained recently in calculations for 0.5 ML of OH_{br} on the surface [23]. Only two earlier studies report values for the Ti-OH_t and Ti-OH_{br} bondlengths coexisting in the dissociated state on the perfect surface; these are 1.87 Å and 2.06 Å [29], and 1.63 Å and 1.87 Å [30], respectively. While the latter pair of values includes at least one that seems unreasonably short, the former are fully consistent with the other more fragmentary results,

and are clearly consistent with our experimental finding that the Ti-OH_t distance is significantly shorter than that of the Ti-OH_{br} bond, with particularly good quantitative agreement for the Ti-O_t bondlength.

A further key parameter in the optimising the agreement between the results of the multiple scattering calculations and our experiments is the fractional coverage of OH_t species. For water dissociation on a perfect TiO_2(110) surface, we expect an equal number of OH_t and OH_{br} species, but it is now well-established that even well-prepared surfaces contain a significant number (typically up to ~10%: we find a value of 6-7% in our study as shown below) of O_{vac} defects, each of which will lead to two OH_{br} species following exposure to water. 30% occupation of OH_t species, as found in our PhD structure optimisation, implies that a further 30% of the OH species are OH_{br} arising from dissociation at perfect areas of the surface, while the remaining 40% of OH_{br} must be associated with defect-site dissociation. In order to estimate the absolute coverages in our experiments we make use of the calibration of the O 1s chemical shift of molecular water as a function of its coverage provided by Ketteler *et al.* [20]; according to this dependence, the chemical shift of 3.5-3.6 eV seen in our data corresponds to a water coverage of approximately 0.25 ML. This is significantly less, but much more reliable and precise, than the rather crude estimate reported previously of 0.45-0.90 ML [18] that was based on the attenuation of the oxidic O 1s and Ti 2p photoemission resulting from the water adsorption. The coverage estimated in this way is not only sensitive to the estimated value of the photoelectron attenuation length, but also to how one defines the 'thickness' of a submonolayer coverage of water; indeed, this approach actually led to estimated thicknesses using the O 1s and Ti 2p attenuations that differed by 50%. We should note, however, that we now see that this earlier coverage estimate was for the combined H_2O/OH surface layer, so in fact the wide range does cover the new value for this combined coverage. In particular, using the coverage value of 0.25 ML for the H_2O obtained from the new calibration of Ketteler *et al.* [20], the measured intensity ratio of the O 1s OH and H_2O signals then leads to an OH coverage of 0.28 ML in the coadsorbed state, and a combined coverage of 0.53 ML.

Using this same calibration, we find the intensity of the OH component after annealing the surface to 370 K (and also of the OH component on the initial 'clean' surface) to be 0.13 ML, indicating an O_{vac} concentration of ~6-7%, close to the value previously reported under

similar preparation conditions [31]. If the OH coverage arising from dissociation on the perfect areas of the surface is (0.28-0.13)=0.15 ML, then the expected OH_t coverage is 0.075 ML, corresponding to 27% of the total OH coverage, in excellent agreement with the figure of 30% obtained from the PhD data analysis.

Of course, there is finite precision in the determination of the OH_t concentration in the PhD analysis, and this we establish by determining how large a change in the parameter is required for the associated *R*-factor to exceed the sum of its minimum value, R_{min}, (for the best-fit structure) and the estimated variance in this minimum value var(R_{min}) [21, 22]. PhD modulations measured in directions that correspond to ~180° backscattering from a nearest-neighbour substrate atom are generally dominated by scattering from this one neighbour, so the normal emission spectrum is expected to have modulations that are most strongly influenced by scattering from the atop species. Using this most-sensitive spectrum to estimate the precision yields a fractional occupation value for the OH_t species of 30(-15/+18)%, clearly excluding the possibility that only OH_{br} species are present. This is illustrated in Fig. 3 which shows comparisons of the experimental PhD spectrum at normal emission with simulations for 0% and 30% OH_t species, together with a plot of the variation of the associated *R*-factor as a function of the fractional occupation value (the horizontal line corresponding to $R = R_{min} + \mathrm{var}(R_{min})$).

In summary, our use of the chemical-state specificity of the PhD technique has allowed us to demonstrate that, at temperatures of ~190-200 K, water adsorption on TiO_2(110) leads to the formation of both OH_t and OH_{br} species coadsorbed with molecular water, whereas only OH_{br} species are formed by reaction of water with O_{vac} defects on the surface. This qualitative result is consistent with predictions of those theoretical calculations that identify a dissociated state on a perfect surface that forms an OH_t + OH_{br} pair of species that may be unable to move apart. Moreover, the Ti-OH bondlengths found for these two species, 1.85±0.08Å (OH_t), and 1.94±0.07 Å (OH_{br}), are also consistent with theoretical calculations.

We should, perhaps, stress that the PhD technique is sensitive only to the *local* geometry of the photoemitting atoms, and particularly to the location of the emitter atom relative to the underlying substrate atoms. It is insensitive to the location of other nearby adsorbed species. Thus, while we clearly identify the local geometry of the OH_t and OH_{br} species, we are unable

to establish whether the OH_t species are always adjacent on the surface to an OH_{br} species (as would be the case in the pseudo-dissociated state) or adjacent on the surface to an intact water molecule to which it may be hydrogen-bonded, as suggested in another theoretical treatment [5]. Similarly, our earlier determination of the local adsorption site of the intact water molecules [17, 18] is not influenced by whether or not water dimers are formed on the surface [32]. These various pairings of coadsorbed species only influence the PhD data if they result in significant changes (such as off-site displacements of greater than ~0.2 Å) in the local sites of the individual species.

However, our results conflict with the results of those more recent theoretical studies indicating no dissociation of water should occur on the perfect TiO_2(110) surface. We should stress, however, that the dissociated state we detect is coexistent with intact molecular water, with only ~30% ([0.15 ML/2]/0.25 ML) of the water molecules adsorbed onto the perfect surface being dissociated; in fact a half-dissociated state was proposed in early DFT calculations [5], and even a very recent study [10] finds this state to be only marginally disfavoured energetically.

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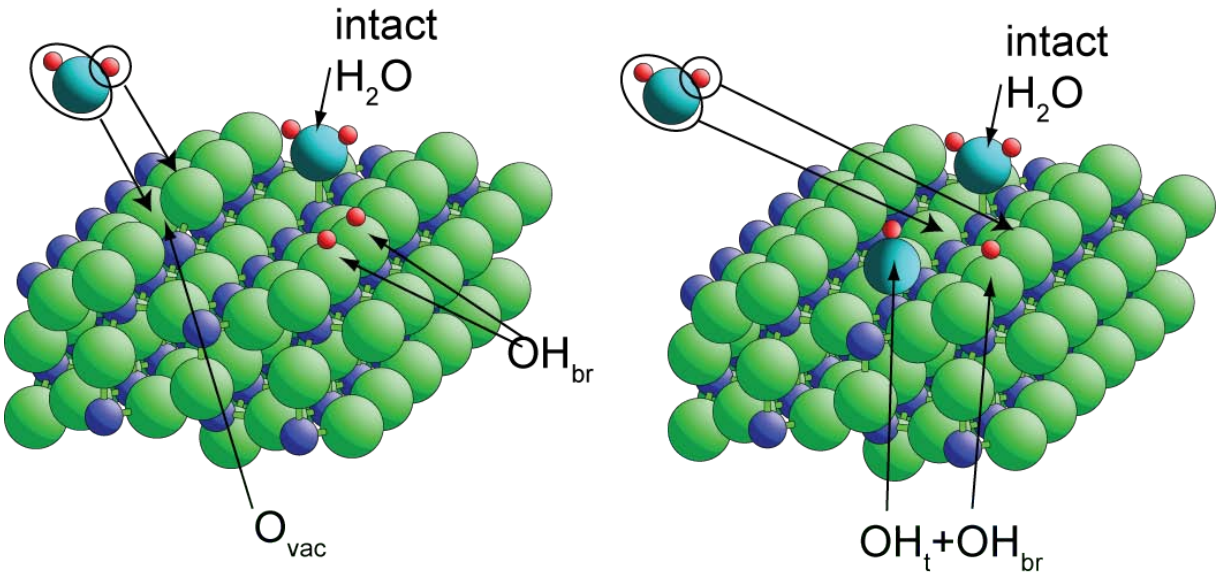

Fig. 1 Schematic diagram of the interaction of molecular H_2O with TiO_2(110) on (left) a surface containing bridging oxygen vacancies, O_{vac}, to produce two bridging hydroxyl species, OH_{br} and (right) on a perfect surface to produce atop and bridging hydroxyl species, OH_t and OH_{br}. The diagrams show both the component parts of a water molecule approaching the dissociation sites, and the resulting pair of surface OH species produced. At low temperatures coadsorbed intact molecular water also occupies Ti-atop sites.

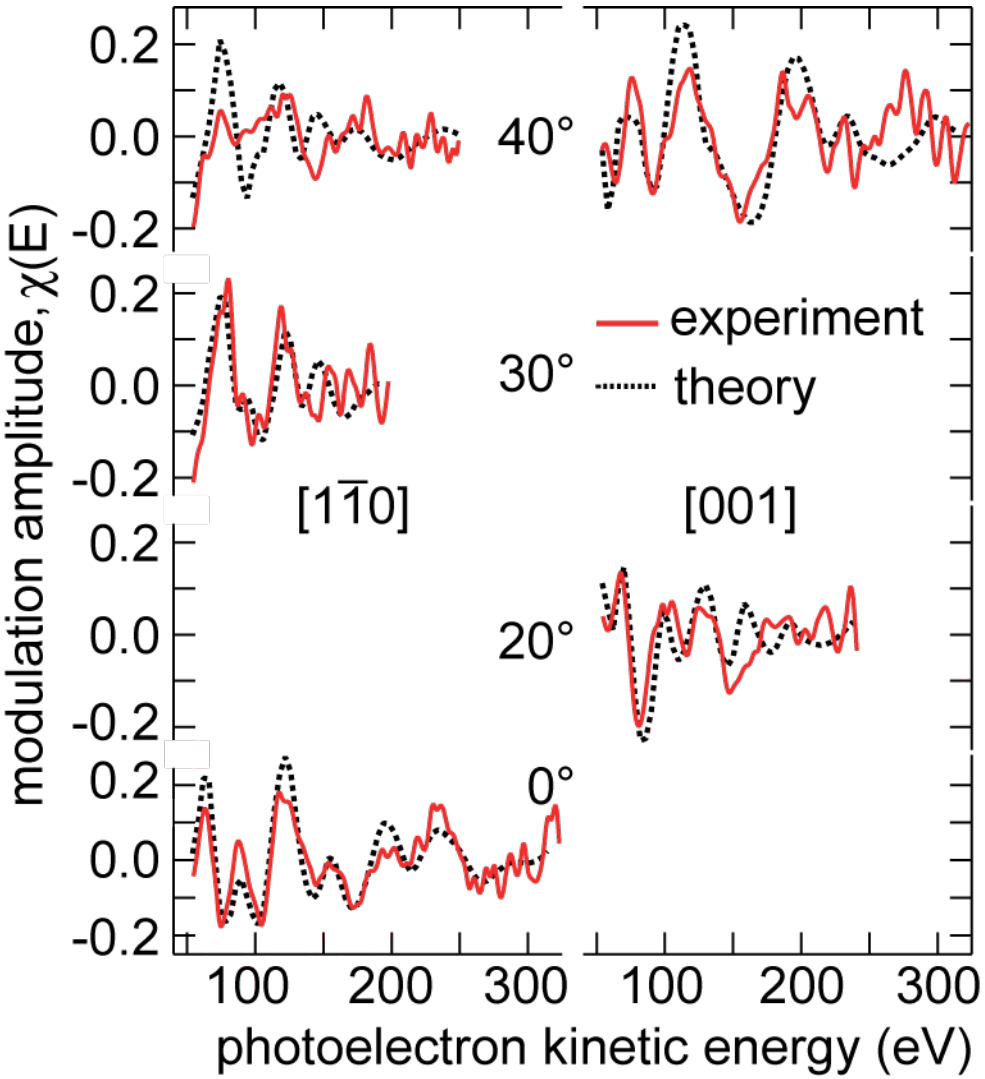

Figure 2: Comparison of the experimental O 1s (OH) PhD spectra with theoretical simulations for the best-fit structure discussed in the text.

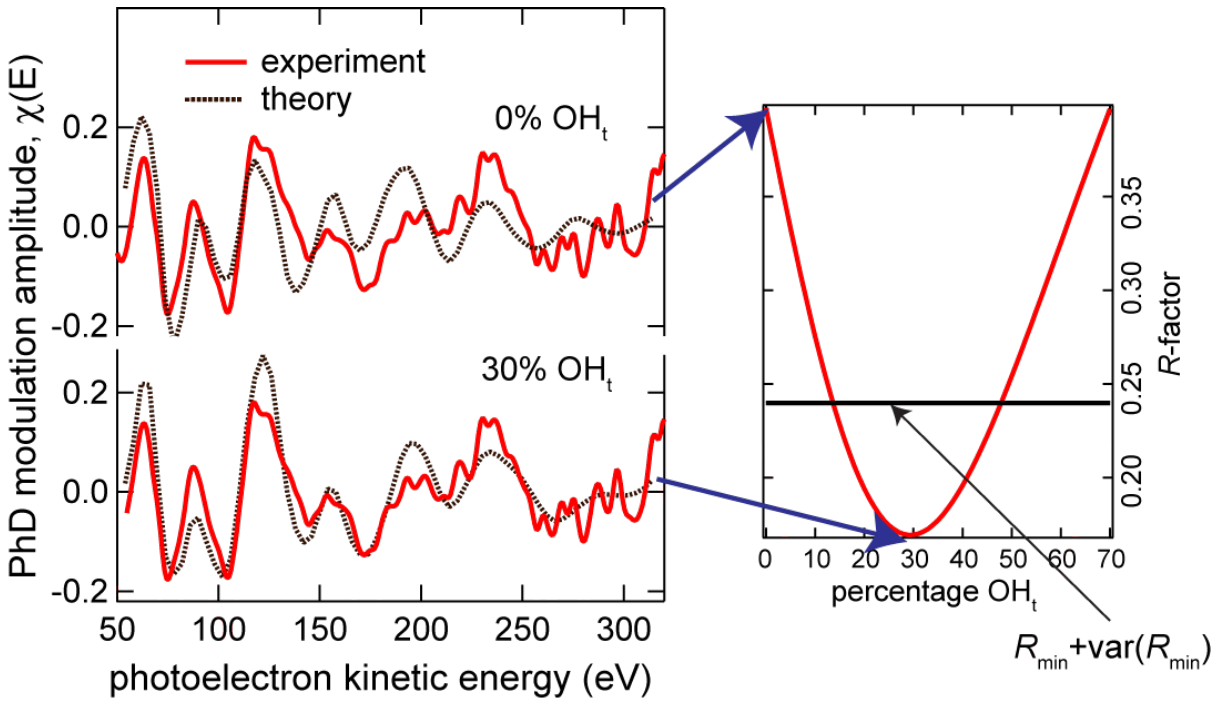

Fig. 3 Dependence of the level of agreement between experiment and theory for the normal emission PhD spectrum as a function of the fractional occupation of OH_t species. On the left are shown theory/experiment comparisons for 0% and 30% OH_t occupation, on the right is shown the dependence of the *R*-factor on this parameter.

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